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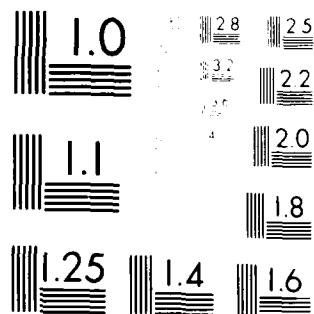
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The Magnitude of Secondary Electron
Contributions in Photon Stimulated Desorption

By

D. E. Ramaker, T. E. Mauey, and R. L. Kurtz and H. Sambe

Prepared for Publication

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The Magnitude of Secondary Electron Contributions in Photon Stimulated Desorption

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1. Introduction

Recent reports on the extent of secondary electron contributions in electron/photon stimulated desorption (ESD/PSD) appear to be contradictory. JAEGER et al. [1] suggested that secondary electrons provide the dominant contribution to the H^+ yield from NH_3/Ni and called the process x-ray induced ESD (XESD). Others have concluded that the XESD process is the dominant mechanism in the PSD of N^+ and O^+ ions from mixed condensed gases such as N_2 and O_2 [2] and in the PSD of H^+ ions from $OH/YbO-Sm$ [3]. On the other hand, considerable evidence exists in the literature for the dominance of the direct photon excitation mechanisms. This evidence usually comes from observed differences between the ion yield and the secondary electron yield or from the absence of any clear structure or "turn on" at certain core levels [4].

It seems clear that the magnitude of the XESD effect is generally not known, but this is an important question. Most helpful in sorting out the complex mechanisms in PSD has been the comparison of the photon energy dependence of the ion spectral yield with constant initial state photoelectron spectra [5]. However, if the ion yield is dominated by effects from the secondary and back-scattered electrons, then this comparison provides no information because the ion yield will simply reflect the bulk DOS, regardless of the excitation involved. Moreover, the usefulness of PSD extended x-ray absorption fine structure (EXAFS) measurements for obtaining information on surface structure [6] will be highly limited if XESD contributions dominate. This paper presents a re-examination [4] of the three systems mentioned above where a dominant XESD effect has been postulated to determine the validity of the conclusions previously reached.

2. H^+ from NH_3/Ni

The H^+ yield spectrum from $NH_3/Ni(110)$, where the NH_3 layer was believed by JAEGER et al. [1] to have an appreciable thickness, reveals the Ni L edge [1]. This suggests that the XESD mechanism must be acting, if indeed all Ni atoms are separated by many NH_3 layers from the outer surface. Furthermore, at the N K edge, the total electron yield (TEY) and H^+ yields are very similar except for the presence of a shoulder in the H^+ yield which is not present in the TEY. This shoulder was interpreted by JAEGER et al. [1] to arise from the direct core level excitation of a surface NH_3 molecule, the remainder of the yield spectrum arising from the XESD mechanism. Based on this interpretation, the XESD process is estimated to cause 60% of the total yield.

Our thermal desorption studies and other data indicate, however, that the thickness of the NH_3 films used by JAEGER et al. [1] were considerably different from those which they reported [4]. We also indicate that the observed shoulder in the H^+ yield arises because the $1s^{-1}4s$ excitation at this energy has a higher branching ratio for the desorption process than for excitation into the Rydberg or continuum orbitals [4]. This is indicated because of the antibonding character of the $4s$ orbital. Thus we do not believe that sufficient evidence has been provided to indicate that the XESD contribution is dominating in this case; indeed, we believe that the difference between the TEY and the H^+ yield provides evidence that it is not dominant.

3. O^+ and N^+ from N_2-O_2

Recently PARKS et al. [2] reported the TEY and O^+ and N^+ yields from a condensed mixture of N_2 and O_2 . The presence of large N^+ and O^+ yields at both the N and O K levels indicates very strongly that the XESD mechanism is playing an important role; indeed, they concluded that the XESD mechanism dominates for N^+ , but is small for O^+ desorption.

PARKS et al. [2] analyzed their data on the basis of absolute quantities, namely on their experimental absolute ion yields and photon fluxes, and on previously reported photoionization cross-sections. The latter in particular are not known very accurately. We prefer to rely on the TEY which they reported, indeed a simple comparison of the TEY and O^+ and N^+ spectral yield curves indicates that the O^+ yield is very similar to the TEY, while the N^+ is very different [4]. This indicates, contrary to the above, that the O^+ yield is dominated by the XESD mechanism, while the N^+ yield is not. A detailed analysis indicates that the XESD cross section for N^+ and O^+ are comparable, but that the direct cross section for N^+ is 20 times that for O^+ [4].

The primary core level dissociation process in diatomics involves Auger decay of the core hole, resulting in a two-hole ($2h$) final state, which directly results in dissociation via a "Coulomb explosion". This Auger stimulated desorption (ASD) mechanism is known to be active in the gas phase [7], and it is believed to be active also in the condensed phase, at least for N_2 and CO [7]. We believe that a similar mechanism is appropriate in the condensed N_2-O_2 mixture, only in this case an electron transfer occurs from a resonant $2\pi^*$ orbital of a neighboring O_2 molecule [4]. This transferred electron screens the two valence holes caused by the Auger decay and thus prevents the ASD process. This electron transfer cannot occur in condensed N_2 because the comparable $2\pi^*$ orbital is empty.

Evidence that this charge transfer process can occur in O_2 comes from visible absorption spectra. Isolated O_2 dimers in a solid neon host have a characteristic absorption spectrum [8] resulting from absorption of a single photon to produce a singlet state in which both halves of the dimer are electronically excited. The electronic energy transfer is believed to result from electron exchange of the $2\pi^*$ electron [8]. Furthermore, recent absorption and photoelectron data on condensed N_2 and O_2 reveal that the $2\pi^*$ band is significantly broadened by normal intermolecular interactions [9]. Finally, direct evidence has been given recently indicating that $2\pi^*$ electron transfer does occur in condensed NO [10].

4. H^+ from $OH-YbO/Sm$

Finally, the H^+ yield from an oxidized Yb surface on a bulk Sm metal substrate shows large features which arise from the Sm and Yb 4d-4f giant resonances [3]. Although little of the Sm surface is thought to be exposed, the Sm feature is much larger than the Yb feature. If indeed the Sm surface is totally covered, this strongly indicates that the XESD process is dominant in this system. The H^+ which desorbs is most likely bonded to the O atoms in the oxidized Yb. The giant resonance, 4d-4fⁿ⁺¹, Auger decays or autoionizes predominantly to 4fⁿ⁺¹, a one-hole valence state which does not lead to desorption. Thus the direct ASD process is inactive at both the Yb and Sm core levels, and the XESD process is expected to dominate [4].

5. Summary

It has been shown for the three systems discussed above that either alternate interpretations of the data are possible, indicating that the XESD effect is not dominant, or that the XESD process dominates only because the direct ASD mechanism is suppressed. This makes the results on these three systems consistent with the significantly larger number of papers, which indicate that the XESD contribution is generally not dominant [4]. We conclude that in cases for which the direct core level ASD process is active, the indirect XESD contribution is generally on the order of 35% or less. The XESD contribution apparently dominates the total yield only in those cases when the direct ASD contribution is suppressed.

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